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BARIUM NITRATE

[10022-31-8]

Formula: $\text{Ba}(\text{NO}_3)_2$; MW 261.37;

Synonym: nitrobarite

Uses

Barium nitrate is used to produce green color in flares, pyrotechnic devices; in green signal lights; and in tracer bullets.

Physical Properties

White cubic crystal; density 3.24 g/cm³; melts at 590°C; soluble in water (5 g and 10.5 g/100 g at 0°C and 25°C, respectively), insoluble in alcohol.

Thermochemical Properties

ΔH°_f	-237.11 kcal/mol
G°_f	-190.42 kcal/mol
S°	51.1 cal/degree mol
C_p	36.2 cal/degree mol

Preparation

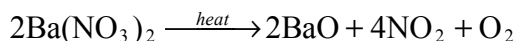
Barium nitrate is prepared by the reaction of barium carbonate or barium sulfide with nitric acid:



Barium carbonate is suspended in nitric acid. The solution is filtered and the product crystallizes out. Alternatively, barium carbonate and nitric acid are added to a saturated solution of barium nitrate. The product is obtained by crystallization. It also may be prepared by adding sodium nitrate to a saturated solution of barium chloride. Barium nitrate precipitates out from the solution. The precipitate is filtered, washed and dried.

Reactions

At elevated temperatures, barium nitrate decomposes to barium oxide, nitrogen dioxide, and oxygen:



In an atmosphere of nitric oxide, thermal decomposition produces barium nitrite, $\text{Ba}(\text{NO}_2)_2$. Reactions with soluble metal sulfates or sulfuric acid yield barium sulfate. Many insoluble barium salts, such as the carbonate, oxalate and phosphate of the metal, are precipitated by similar double decomposition reactions. $\text{Ba}(\text{NO}_3)_2$ is an oxidizer and reacts vigorously with common reducing agents. The solid powder, when mixed with many other metals such as aluminum or zinc in their finely divided form, or combined with alloys such as

aluminum-magnesium, ignites and explodes on impact.

Analysis

Elemental composition: Ba 52.55%, N 10.72%, O 36.73%. Barium may be determined by various instrumental techniques (see Barium). The nitrate ion can be determined by preparing an aqueous solution of the compound and analyzing by ion-chromatography, or nitrate ion-selective electrode.

Toxicity

Barium nitrate exhibits high-to-moderate toxicity by oral, subcutaneous and other routes. The oral lethal dose in rabbit is 150 mg/kg and the oral LD₅₀ in rat is 355 mg/kg (Lewis Sr., R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed., New York: Van Nostrand Reinhold).

BARIUM OXIDE

[1304–28–5]

Formula: BaO; MW 153.33

Synonyms: calcined baryta; barium monoxide; barium protoxide.

Uses

Barium oxide is used to remove water from alcohols, aldehydes, ketones, petroleum ether, and other organic solvents; and for drying gases. It also is used in the manufacture of detergent for lubricating oil.

Physical Properties

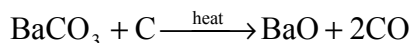
Colorless cubic crystal or white yellowish powder; density 5.72 g/cm³; melts at 2,013°C; moderately soluble in water at ambient temperatures (3.48 g/ 100 g at 20°C), highly soluble in boiling water (90.8 g/100 g at 100°C); aqueous solution highly alkaline; also, soluble in ethanol, dilute mineral acids and alkalies; insoluble in acetone and liquid ammonia.

Thermochemical Properties

$\Delta H^{\circ}f$	–132.35 kcal/mol
$\Delta G^{\circ}f$	–125.56 kcal/mol
S°	16.8 cal/degree mol
C_p	11.4 cal/degree mol
ΔH_{fus}	14.1 kcal/mol

Preparation

Barium oxide is made by heating barium carbonate with coke, carbon black or tar:



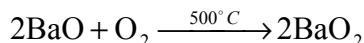
It may be also prepared by thermal decomposition of barium nitrate.

Reactions

Barium oxide reacts with water forming hydroxide, and with carbon dioxide it forms barium carbonate. Both reactions are rapid and exothermic:



It readily forms barium peroxide BaO_2 when heated in air or oxygen at 450°C to 500°C :



When heated with silica to incandescence, it forms monobarium silicate, $\text{BaO} \cdot \text{SiO}_2$ or Ba_3SiO_5 .

Aqueous solution of barium oxide undergoes neutralization reactions with acids forming precipitates of insoluble barium salts, such as BaSO_4 and $\text{Ba}_3(\text{PO}_4)_2$.

BaO reacts slowly with alcohols forming barium alcoholates.

Analysis

Elemental composition: Ba 89.57%, O 10.43%. The oxide is identified by x-ray diffraction and barium content determined by AA or ICP.

Hazard

Barium oxide is toxic by subcutaneous route. Because of its affinity for moisture, the compound is corrosive to skin. Contact with water or CO_2 evolves much heat. Therefore, any use of CO_2 to extinguish a BaO fire may cause further incandescence. Accumulation of barium oxide or peroxide dust can create a fire hazard.

BARIUM PEROXIDE

[1304–29–6]

Formula: BaO_2 ; MW 169.33

Synonyms: barium dioxide; barium superoxide.

Uses

Barium peroxide is used as a bleaching agent for fibers and straw. It also is used to decolorize glass; in dyeing textiles; to produce pure oxygen; to prepare hydrogen peroxide; and as an oxidizing agent.

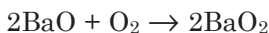
Physical Properties

Grayish-white, heavy powder; tetragonal crystal system; density 4.96 g/cm^3 ; melts at 450°C ; insoluble in water.

Preparation

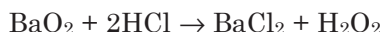
Barium peroxide is prepared by heating barium oxide with air or oxygen at

500°C:



Reactions

Barium peroxide decomposes to barium oxide and oxygen when heated to 700°C. At lower temperatures, decomposition occurs slowly. It also decomposes slowly in contact with water, forming barium hydroxide. It reacts with dilute acids to form hydrogen peroxide:



Analysis

Elemental composition: Ba 81.11%, O 18.89%. The compound is decomposed by dilute HCl and the barium content by AA or ICP-AES.

Hazard

Barium peroxide may ignite or explode in contact with reducible substances. Also, it is toxic by the subcutaneous route.

LD₅₀ subcutaneous (mouse): 50 mg/kg

BARIUM SULFATE

[7727-43-7]

Formula: BaSO₄; MW 233.39

Synonyms: barite; baryte; heavy spar; blanc fixe

Occurrence and Uses

Barium sulfate is widely distributed in nature and occurs as the mineral barite (also known as barytes or heavy spar). It often is associated with other metallic ores, such as fluorspar. Barites containing over 94% BaSO₄ can be processed economically.

Barium sulfate has many commercial applications. It is used as natural barite, or precipitated BaSO₄. The precipitated salt in combination with equimolar amount of co-precipitated zinc sulfide formerly was used as a white protective coating pigment, known as lithophone. Similarly, in combination with sodium sulfide, it is used to produce fine pigment particles of uniform size, known as blanc fixe. Natural barite, however, has greater commercial application than the precipitated salt. It is used as drilling mud in oil drilling to lubricate and cool the drilling bit, and to plaster the walls of the drill hole to prevent caving. It is used as a filler in automotive paints, plastics and rubber products. It also is used in polyurethane foam floor mats; white sidewall rubber tires; and as a flux and additive to glass to increase the refractive index.

Other chemical applications of barium sulfate are as the opaque ingredient in a barium meal for x-ray diagnosis; as a pigment for photographic paper; and to prepare many barium salts.

Physical Properties

Soft crystalline solid; rhombic crystal; pure salt is white but color may vary; the color of the mineral barite may vary among red, yellow, gray or green depending on impurities; density 4.50 g/cm³; refractive index 1.64; melts around 1,580°C; decomposes above 1,600°C; hardness 4.3 to 4.6 Mohs; insoluble in water (285 mg/L at 30°C) and alcohol; K_{sp} 1.1×10^{-10} ; soluble in concentrated sulfuric acid.

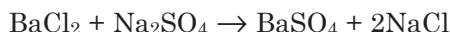
Thermochemical Properties

ΔH°_f	-352.3 kcal/mol
ΔG°_f	-325.7 kcal/mol
S°	31.6 cal/degree mol
C_p	24.3 cal/degree mol
ΔH_{fus}	9.71 kcal/mol

Production

Natural barium sulfate or barite is widely distributed in nature. It also contains silica, ferric oxide and fluoride impurities. Silica is the prime impurity which may be removed as sodium fluorosilicate by treatment with hydrofluoric acid followed by caustic soda.

Very pure barium sulfate may be precipitated by treating an aqueous solution of a barium salt with sodium sulfate:

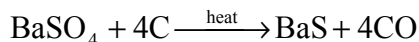


Precipitated BaSO₄ is often used in many industrial applications. Blanc fixe and Lithopone are made by the reactions of barium sulfide with sodium sulfate and zinc sulfate, respectively.

Reactions

Barium sulfate is one of the most insoluble salts of barium. It does not undergo double decomposition reactions in aqueous phase. It dissolves in concentrated H₂SO₄ to form an acid sulfate which breaks down to BaSO₄ upon dilution.

Reduction with coke under heating produces barium sulfide:



BaSO₄ reacts violently when heated with aluminum or explosively when mixed with potassium.

Analysis

Elemental composition: Ba 58.84%, O 27.42%, S 13.74%. Barite may be identified by x-ray diffraction. The metal may be analyzed by various instrumental techniques (see Barium).

BARIUM SULFIDE

[21109-95-5]

Formula: BaS; MW 169.39

Barium also forms several other sulfides. Among them are: Barium hydrosulfide, Ba(SH)₂ [25417-81-6]; Barium disulfide, BaS₂ [12230-99-8]; Dibarium trisulfide, Ba₂S₃ [53111-28-7]; Barium trisulfide, BaS₃ [12231-01-5]; Barium tetrasulfide monohydrate, BaS₄·H₂O [12248-67-8]; Barium pentasulfide, BaS₅ [12448-68-9].

Occurrence and Uses

Barium sulfide occurs in the form of black ash, which is a gray to black impure product obtained from high temperature carbonaceous reduction of barite. It is the starting material in the manufacture of most barium compounds including barium chloride and barium carbonate. It is used in luminous paints; for dehairing hides; as a flame retardant; and for generating H₂S.

Physical Properties

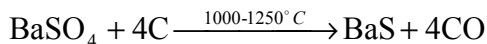
Colorless crystalline solid; density 4.25 g/cm³; refractive index 2.155; melts at 1,200°C; soluble in water (decomposes); insoluble in alcohol.

Thermochemical Properties

$\Delta H^{\circ}f$	-110 kcal/mol
$\Delta G^{\circ}f$	-109 kcal/mol
S°	18.7 cal/degree mol
C_p	11.8 cal/degree mol

Preparation

Barium sulfide is prepared by heating barite with coal or petroleum coke in a rotary kiln at 1,000°C to 1,250°C in an oxygen-free atmosphere:



The product, black ash, is a gray or black powder containing carbonaceous impurities and unreacted barite. Barium sulfide is separated from impurities by extraction with hot water and filtration. It is obtained as an aqueous solution of 15 to 30% strength. The commercial product is 80% to 90% BaS.

Barium sulfide may also be made by high temperature reduction of barium sulfate with methane.

Reactions

Barium sulfide dissolves in water, dissociating to 10%, forming barium hydrosulfide and barium hydroxide:



The solution is highly alkaline. When the aqueous solution is cooled, crystals of barium hydroxide appear first.

The aqueous solution of barium sulfide oxidizes slowly in the air forming elemental sulfur and various anions of sulfur including sulfite, thiosulfate, polysulfides and sulfate. The yellow color of barium sulfide solution is attributed to the presence of dissolved elemental sulfur that results from its slow oxidation in the air. In the presence of an oxidizing agent, barium sulfate is formed. Violent to explosive oxidation may occur when heated with strong oxidants such as phosphorus pentoxide or potassium chlorate.

Barium sulfide undergoes double decomposition reactions with hydrochloric acid and nitric acid, giving barium chloride and barium nitrate, respectively, when the solution is evaporated.

Reaction with carbon dioxide produces barium carbonate and hydrogen sulfide:



Analysis

Elemental composition: Ba 81.08%, S 18.92%. The metal may be analyzed by various instrumental techniques (see Barium). In the powder form, the compound may be identified by x-ray methods. In solution, it undergoes hydrolysis forming barium hydroxide and hydrosulfide. The former is neutralized by acid titration to a pH of 8.4 while the hydrosulfide is titrated with acid to pH 4.2 for neutralization.

Toxicity

Highly toxic by ingestion (see Barium).

BARIUM TITANATE

[12047-27-7]

Formula: BaTiO_3 ; MW 233.19

Synonyms: barium metatitanate; barium titanate (IV)

Uses

Barium titanate has many important commercial applications. It has both ferroelectric and piezoelectric properties. Also, it has a very high dielectric constant (about 1,000 times that of water). The compound has five crystalline modifications, each of which is stable over a particular temperature range. Ceramic bodies of barium titanate find wide applications in dielectric amplifiers, magnetic amplifiers, and capacitors. These storage devices are used in digital calculators, radio and television sets, ultrasonic apparatus, crystal microphone and telephone, sonar equipment, and many other electronic devices.

Physical Properties

White crystalline solid; exists in five crystal modifications; the common

tetragonal form has a Curie point of 120°C; exhibits ferroelectric and piezoelectric properties; density 6.02 g/cm³; melts at 1,625°C; insoluble in water and alkalis; slightly soluble in dilute mineral acids; dissolves in concentrated sulfuric acid and hydrofluoric acid.

Preparation

Barium titanate is made by sintering a finely powdered mixture of barium carbonate and titanium dioxide in a furnace at 1,350°C. The calcined mass is finely ground and mixed with a binder (plastic). The mixture is subjected to extrusion, pressing or film casting to obtain ceramic bodies of desired shapes. Plastic is burnt off by heating and the shaped body is sintered by firing and then polished.

The compound also may be prepared by other methods. These include ignition of barium and titanium alcoholates in an organic solvent; treatment of tetraethyl titanate or other alkyl ester of titanium with an aqueous solution of barium hydroxide; and ignition of barium titanyl oxalate.

Analysis

Elemental composition: Ba 58.89%, Ti 20.53%, O 20.58%. The solid is digested with a mixture of concentrated H₂SO₄ and HNO₃, diluted and the aqueous solution is analyzed for the metals Ba and Ti by flame or furnace atomic absorption or ICP emission spectrophotometry. The compound in the crystalline powdered form may be identified by various x-ray techniques.

BERKELIUM

[7440-71-3]

Symbol Bk; atomic number 97; atomic weight of most stable isotope 247.07; a transuranium radioactive element; synthesized in the laboratory; electronic configuration [Rn]5f⁹7s²; oxidation states +3 and +4. Isotopes, half-life and decay modes are given below:

Isotopes	Half-Life	Decay Mode
Bk-241	2.4 min.	electron capture
Bk-242	7 min.	electron capture
Bk-243	4.5 hr.	electron capture
Bk-244	4.4 hr.	electron capture
Bk-245	4.95 days	electron capture
Bk-246	1.8 days	electron capture
Bk-247	1,400 years	alpha particle emission
Bk-248	23.7 hr.	beta decay, electron capture
Bk-249	320 days	beta decay
Bk-250	3.2 hr.	beta decay
Bk-251	56 min.	beta decay

Occurrence and Uses

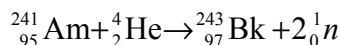
Berkelium does not occur in nature. The element was synthesized in 1949 at the Lawrence Berkeley Laboratory in Berkeley, California by Thompson, Ghiorso and Seaborg (Thompson, S.G., Ghiorso, A. and G. T. Seaborg. 1950. *Phys. Rev.*, 77, 838). It has 12 isotopes. It is the fifth man-made transuranium element. Presently, the element has no commercial application.

Physical Properties

Physical properties of the element are anticipated or calculated. Silvery metal having two allotropic forms: (i) alpha form that should have a double hexagonal closed-packed structure and (ii) a face-centered cubic type beta form; density 14.78 g/cm³ (alpha form), and 13.25 g/cm³ (beta form); melting point 985°C; soluble in dilute mineral acids.

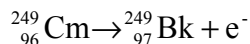
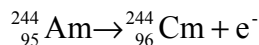
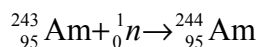
Synthesis

All isotopes of the element are synthesized in the nuclear reactor. The first isotope synthesized had the mass 241, produced by irradiation of milligram quantities of americium-241 with alpha particles of 35 MeV in a cyclotron:



The product was separated by ion exchange.

While the lighter isotopes are prepared by alpha particle bombardment, the heavier ones by neutron irradiation of large quantities of americium, curium or plutonium:



Only a small fraction of Bk-249 is obtained by the above reaction because neutrons also induce fission. Alternatively, uranium-238 may be converted to Bk-249 by very short but intense neutron bombardment followed by five successive beta decays.

Chemical Properties

The chemical properties of berkelium are rare earth-like character because of its half-filled 5*f* subshell and should be similar to cerium. The element readily oxidizes to berkelium dioxide, BkO₂ when heated to elevated temperatures (500°C). In aqueous solutions, the most common oxidation state is +3 which may undergo further oxidation to +4 state. A few compounds have been synthesized, the structures of which have been determined by x-ray diffraction methods. These include the dioxide, BkO₂; sesquioxide, Bk₂O₃; fluoride,

BkF_3 ; chloride, BkCl_3 ; oxychloride, BkOCl ; and the hydroxides, Bk(OH)_3 and Bk(OH)_4 .

Toxicity

Berkelium accumulates in the skeletal system. The radiation can cause damage to red blood cells. The maximum permissible body burden reported for the isotope Bk-249 in the human skeleton is 0.4 ng (Cunningham, B.B., 1968, Berkelium. In *The Encyclopedia of the Chemical Elements*. C.A. Hampel, ed., p. 48. New York: Reinhold Book Corporation).

BERYLLIUM

[7440-41-7]

Symbol Be; atomic number 4; atomic weight 9.012; a Group IIA (Group 2) metal; the lightest alkaline-earth metallic element; atomic radius 1.06Å; ionic radius (Be^{2+}) 0.30Å; electronic configuration $1s^2 2s^2$; ionization potential, Be^+ 9.32eV, Be^{2+} 18.21 eV; oxidation state +2

Occurrence and Uses

Beryllium is widely distributed in the earth's crust at trace concentration, 2.8 mg/kg. The element was first discovered by Vauquelin in 1797. Wohler and Bussy in 1828 independently isolated beryllium in the metallic form from its oxide. In nature, beryllium occurs in several minerals, mostly combined with silica and alumina. The most common minerals are beryl, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$; chrysoberyl, $\text{BeO} \cdot \text{Al}_2\text{O}_3$; phenacite, $2\text{BeO} \cdot \text{SiO}_2$; and bertrandite, $4\text{BeO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$. Also, it is found in trace amounts in the ore feldspar, and in volcanic ash. Its abundance in the sea water is estimated in the range 5.6 ppt.

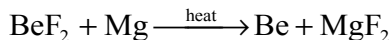
Beryllium oxide is a component of precious stones, emerald, aquamarine and topaz. Beryllium is utilized in nuclear reactors to moderate the velocity of slow neutrons. It is hot-pressed to appropriate shapes and sizes that yield high strength and ductility for its applications.

Production

Metallic beryllium is produced by reduction of beryllium halide with sodium, potassium or magnesium. Commercially, it is obtained primarily from its ore, beryl. Beryllium oxide is separated from silica and alumina in ore by melting the ore, quenching the solid solution, and solubilizing in sulfuric acid at high temperatures and pressure. Silica and alumina are removed by pH adjustment. Beryllium is converted to its hydroxide. Alternatively, beryl is roasted with complex fluoride. The products are dissolved in water and then pH is adjusted to produce beryllium hydroxide.

The impure hydroxide obtained above is purified by converting to a double salt, ammonium beryllium fluoride, which subsequently, on thermal decomposition, gives beryllium fluoride. The latter is heated with magnesium metal

to form pure beryllium metal:



It finally is purified by either vacuum melting or chelation with an organophosphate reagent followed by liquid-liquid extraction.

Beryllium halide alternatively may be reduced to the metal or converted to alloy by electrolysis.

Physical Properties

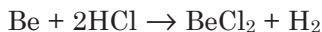
Grayish metal; hexagonal close-packed crystal system, lattice constant, $a=2.286 \text{ \AA}$ and $c=3.584 \text{ \AA}$; density 1.85 g/cm^3 ; permeable to x-rays; highly ductile; modulus to weight ratio very high, elastic modulus 44.5×10^6 at 25°C (for hot-pressed block and sheet); melting point $1,287^\circ\text{C}$; vaporizes at $2,471^\circ\text{C}$; sound transmission velocity $12,600 \text{ m/sec}$; reflectivity (white light) 55%; thermal neutron absorption cross-section $0.0090 \text{ barns/atom}$; electrode potential, $\text{Be/Be}^{2+}(\text{aq})$ 1.85 V ; electrical resistivity $3.36 \times 10^{-10} \text{ ohm.m}$ (at 20°C).

Thermochemical Properties

Specific heat (at 25°C)	0.436 cal/g $^\circ\text{C}$
ΔH_{fus}	210 cal/g
ΔH_{vap}	5917 cal/g
Coefficient of linear expansion, (at 25°C)	$11.3 \times 10^{-6} / ^\circ\text{C}$
Thermal conductivity, (at 27°C)	2.00 W/cm K

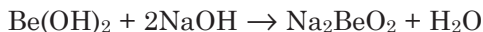
Reactions

Most chemical reactions of beryllium are similar to those of aluminum and, to a lesser extent, magnesium. In general, all the common mineral acids attack beryllium forming their corresponding salts with evolution of hydrogen:



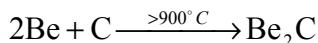
Cold, concentrated nitric acid, however, has no effect when mixed with the metal.

Reactions with alkalis first produce insoluble beryllium hydroxide with evolution of hydrogen. Excess alkali converts the hydroxide to water-soluble beryllate:



Beryllium does not react with oxygen at ordinary temperatures and normal atmosphere. When heated above 700°C , the metal combines with nitrogen, (in an oxygen-free atmosphere) forming beryllium nitride, Be_3N_2 .

Beryllium combines with carbon when heated above 900°C in the absence of air to form beryllium carbide.



Beryllium reacts incandescently with fluorine or chlorine, producing beryllium fluoride or chloride.

Analysis

Elemental Be may be analyzed in acidified aqueous solutions at trace concentrations by flame or furnace atomic absorption spectrophotometer. Also, the analysis may be performed by ICP emission spectrophotometry. In both the furnace-AA and the ICP spectrometry, concentrations at the low ppb levels in aqueous matrices may be analyzed accurately. Be may be measured at an even lower detection level (low ppt) by ICP-mass spectrometry. In the absence of these instruments, the element in aqueous matrices may be analyzed at low ppb levels by colorimetry. An aluminum (aurintricarboxylic acid triammonium salt) buffer reagent is added to aqueous sample to form a beryllium lake and the color developed is measured at 515 nm by spectrophotometer or filter photometer. A small amount of ethylenediamine tetraacetic acid is added as a complexing agent to prevent interference from other metals in the analysis. (APHA, AWWA and WEF, 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association.) The element in solid matrix is brought into solution by heating and digesting with nitric acid.

The metal also may be analyzed in solid matrices by nondestructive methods such as x-ray diffraction or x-ray fluorescence techniques.

Toxicity

Elemental Be and its compounds are very poisonous by inhalation or intravenous route. Chronic inhalation of beryllium dusts or fumes can cause a serious lung disease, berylliosis, after a latent period ranging from several months to many years. Inhalation of airborne dusts can also cause an acute disease manifested as dyspnea, pneumonitis and tracheobronchitis with a short latency period of a few days. Skin contact with soluble salts of the metal can cause dermatitis. Beryllium also is a carcinogen. There is sufficient evidence of its inducing cancer in animals and humans.

It is one of the US EPA's listed priority pollutant metals in the environment.

BERYLLIUM CARBIDE

[506-66-1]

Formula: Be_2C ; MW 30.035

Uses

Beryllium carbide is used in a nuclear reactor as core material.

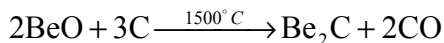
Physical Properties

Red cubic crystal; hard and refractory; density 1.90 g/cm³; decomposes

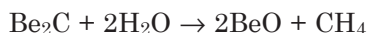
when heated above 2,100°C; reacts with water.

Preparation

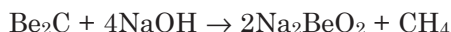
Beryllium carbide is prepared by heating the elements beryllium and carbon at elevated temperatures (above 900°C). It also may be prepared by reduction of beryllium oxide with carbon at a temperature above 1,500°C:



Beryllium carbide decomposes very slowly in water:



The rate of decomposition is faster in mineral acids with evolution of methane. However, in hot concentrated alkalies the reaction is very rapid, forming alkali metal beryllate and methane:



Analysis

Elemental composition: Be 60.02%, C 39.98%. Beryllium may be analyzed by various instrumental techniques (see Beryllium). Additionally, the compound may be treated with a dilute mineral acid. The product methane gas slowly evolved is then analyzed by GC equipped with a TCD, or by GC/MS.

BERYLLIUM CHLORIDE

[7787-47-5]

Formula: BeCl_2 ; MW 79.92

Uses

Beryllium chloride, an electron-deficient compound similar to aluminum chloride, is a Lewis acid. The anhydrous salt is used as a catalyst in organic reactions. Its applications, however, are limited.

Physical Properties

White or yellowish orthorhombic crystal; hygroscopic; density 1.90 g/cm³; melts at 399°C; vaporizes at 482°C; sublimes in vacuum (at ~2 torr) at 300°C; highly soluble in water; moderately soluble in alcohol, ether and pyridine; insoluble in benzene, chloroform, acetone and ammonia.

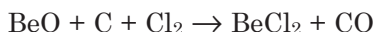
Thermochemical Properties

ΔH°_f	-117.3 kcal/mol
ΔG°_f	-106.6 kcal/mol
S°	19.6 cal/degree mol

C_p	15.5 cal/degree mol
ΔH_{fus}	2.07 kcal/mol
ΔH_{vap}	25.1 kcal/mol

Preparation

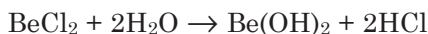
Beryllium chloride is prepared by passing chlorine over beryllium oxide and carbon:



It also is made by combination of beryllium with chlorine.

Reactions

Beryllium chloride is stable in dry air, but absorbs moisture forming tetrahydrate, $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$. It readily dissolves in water undergoing hydrolysis and evolving hydrogen chloride:



Cold aqueous solution of BeCl_2 reacts with H_2S forming beryllium sulfide, BeS , which decomposes on heating.

Toxicity

Highly toxic by ingestion (see Beryllium); LD_{50} oral (rat): 86 mg/kg. It is a confirmed carcinogen and can cause an adverse reproductive effect.

Analysis

Elemental composition: Be 11.28%, Cl 88.72%. Beryllium may be analyzed in aqueous solution or in solid form by different instrumental techniques (see Beryllium). Chloride may be measured in aqueous solution (after appropriate dilution) by titration with a standard solution of silver nitrate or mercuric nitrate; or by ion chromatography or a selective chloride ion electrode.

BERYLLIUM FLUORIDE

[7787-49-7]

Formula: BeF_2 ; MW 47.01

Uses

Beryllium fluoride is the intermediate compound in the magnesium-reduction process to produce beryllium metal. The compound also is used in the manufacture of glass, and in nuclear reactors.

Physical Properties

Glassy solid; tetragonal crystal system; hygroscopic; density 2.1 g/cm³; melts

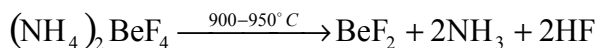
at 552°C; vaporizes at 1,169°C; very soluble in water; sparingly soluble in alcohol.

Thermochemical Properties

$\Delta H^{\circ}f$	-245.5 kcal/mol
$\Delta G^{\circ}f$	-234.2 kcal/mol
S°	12.77 cal/degree mol
C_p	12.39 cal/degree mol
ΔH_{fus}	1.14 kcal/mol

Preparation

Beryllium fluoride is made by thermal decomposition of ammonium beryllium fluoride at 900 to 950°C:



Analysis

Elemental composition: Be 19.17%, F 80.83%. The metal is analyzed by instrumental techniques (see Beryllium), and fluoride may be determined in the aqueous solution by a selective fluoride ion electrode.

Toxicity

Highly toxic by all routes of exposure and also a carcinogen:

LD₅₀ oral (mouse): 100 mg/kg; LD₅₀ subcutaneous (mouse): 20 mg/kg.

BERYLLIUM HYDRIDE

[7787-52-2]

Formula: BeH₂; MW 11.03

Uses

Beryllium hydride has few commercial applications. It is used in rocket fuels.

Physical Properties

White amorphous solid; density 0.65 g/cm³; decomposes at 250°C; reacts with water.

Preparation

Beryllium hydride is made by treating an ethereal solution of beryllium borohydride with triphenylphosphine, or by pyrolysis of di-*tert*-butylberyllium.

Reactions

Beryllium hydride reacts with water, dilute acids, and methanol, liberating

hydrogen. The reactions with acids are violent, presenting a fire risk. Also, it reacts violently with oxidizing agents and organic matter. It decomposes, rapidly liberating hydrogen when heated at 220°C.

BERYLLIUM HYDROXIDE

[13327–32–7]

Formula $\text{Be}(\text{OH})_2$; MW 43.03 Synonym: beryllium hydrate

Uses

Beryllium hydroxide is used to produce beryllium oxide and other beryllium compounds.

Physical Properties

Crystalline solid or amorphous powder; exists in two forms, alpha and beta forms; the alpha form is a granular powder; the beta form is a gelatinous mass of indefinite composition; density 1.92 g/cm³; decomposes to beryllium oxide when heated at elevated temperatures (decomposition commences at 190°C and completes at red heat); practically insoluble in water and dilute alkalis; soluble in acids and hot concentrated caustic soda solution.

Thermochemical Properties

ΔH°_f	–215.8 kcal/mol
ΔG°_f	–194.9 kcal/mol
S°	12.4 cal/degree mol

Preparation

Beryllium hydroxide is prepared by treating basic beryllium acetate, $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ with caustic soda solution; or by precipitation from a strongly alkaline solution of sodium beryllate. The precipitate is dried at 100°C.

Toxicity

The compound is poisonous by intravenous route and a carcinogen; intravenous lethal dose in rat is about 4 mg/kg.

BERYLLIUM NITRATE TRIHYDRATE

[13597–99–4]

Formula: $\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; MW 187.07

Uses

$\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ is used to produce beryllium oxide; and as a mantle hardener in incandescent acetylene or other gas lamps.

Physical Properties

White or yellowish crystalline solid; deliquescent; melts at 60°C; decomposes on further heating; very soluble in water, moderately soluble in alcohol.

Preparation

Beryllium nitrate is made by dissolving beryllium oxide or hydroxide in concentrated nitric acid, followed by crystallization. Also, it may be prepared by mixing beryllium sulfate and barium nitrate solutions followed by evaporation and crystallization.

Analysis

Elemental composition: Be 4.82%, N 14.97%, H 3.23%, O 76.98%

Toxicity

$\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ is toxic by subcutaneous, intravenous and intraperitoneal routes; and also is a carcinogen. LD₅₀ intraperitoneal (mouse): 5 mg/kg

BERYLLIUM NITRIDE

[1304–54–7]

Formula: Be_3N_2 ; MW 55.05

Uses

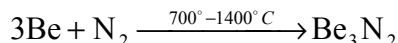
Beryllium nitride is used in nuclear reactors; and to produce radioactive carbon-14 isotope for tracer applications.

Physical Properties

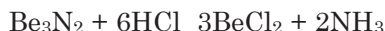
Gray cubic crystal; hard and refractory; density 2.71 g/cm³; melts at 2,200°C; decomposes in acid or alkali; slowly reacts with water.

Preparation

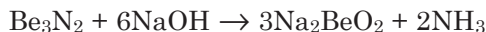
Beryllium nitride may be prepared by heating beryllium metal powder with dry nitrogen in an oxygen-free atmosphere above 700°C:

**Reactions**

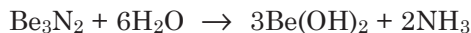
Beryllium nitride reacts with mineral acids producing ammonia and the corresponding salts of the acids:



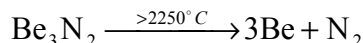
In strong alkali solutions, a beryllate forms, with evolution of ammonia:



Both the acid and alkali reactions are brisk and vigorous. Reaction with water, however, is very slow:



When heated above its melting point, it vaporizes first, and then on further heating dissociates to its elements:



Reactions with oxidizing agents are likely to be violent. It is oxidized when heated at 600°C in air.

Analysis

Elemental composition: Be 49.11%, N 50.89%. Analysis may be performed by treatment with HCl. The soluble BeCl_2 solution is then measured for Be by AA or ICP techniques. The ammonia liberated is determined by titrimetry, colorimetry or by ammonia-selective electrode (see Ammonia).

BERYLLIUM OXIDE

[1304–56–9]

Formula: BeO ; MW 25.01

Synonym: beryllia

Uses

Beryllium oxide shows excellent thermal conductivity, resistance to thermal shock, and high electrical resistance. Also, it is unreactive to most chemicals. Because of these properties the compound has several applications. It is used to make refractory crucible materials and precision resistor cores; as a reflector in nuclear power reactors; in microwave energy windows; and as an additive to glass, ceramics and plastics.

Physical Properties

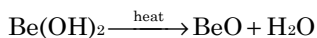
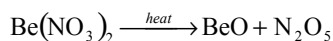
White amorphous powder; density 3.02 g/cm³; hardness 9 Mohs; melts at 2,507°C; vaporizes at 3,900°C; insoluble in water; dissolves slowly and sparingly in concentrated acids and concentrated aqueous solutions of alkalis.

Thermochemical Properties

ΔH°_f	–145.72 kcal/mol
ΔG°_f	–138.7 kcal/mol
S°	3.30 cal/degree mol
C_p (at 100° C)	7.48 cal/degree mol
ΔH_{fus}	20.36 kcal/mol

Preparation

Beryllium oxide is obtained by thermal dissociation of beryllium nitrate or hydroxide:



Also, it may be prepared by heating beryllium sulfate at elevated temperatures. Dissociation begins at 550°C and completes at 1,000°C.

Analysis

Elemental composition: Be 36.03%, O 63.97%. The solid powder may be characterized by x-ray techniques. The metal can be analyzed by microwave-assisted, strong acid digestion followed by flame or furnace AA or ICP spectrophotometric determination.

Toxicity

Chronic inhalation of the powder can cause cancer and adverse reproductive effects.

BERYLLIUM SULFATE

[13510–49–1]

Formula: $\text{Be}(\text{SO}_4)_2$; MW 105.08; also forms a tetrahydrate $\text{Be}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [7787–56–6] (MW 177.14)

Uses

No major commercial application of beryllium sulfate is known.

Physical Properties

Colorless crystalline solid; tetragonal crystal system; hygroscopic; density 2.50 g/cm³ (tetrahydrate 1.71 g/cm³); tetrahydrated salt loses water of crystallization on heating; further heating to 550°C causes decomposition; soluble in water, tetrahydrate more soluble in water (30.5g/100g at 30°) than the anhydrous salt; insoluble in alcohol.

Thermochemical Properties

ΔH°_f	–288.2 kcal/mol
ΔG°_f	–261.5 kcal/mol
S°	18.63 cal/degree mol
C_p	20.49 cal/degree mol

Preparation

Beryllium sulfate may be prepared by treating an aqueous solution of any beryllium salt with sulfuric acid, followed by evaporation of the solution and

crystallization. The hydrated product may be converted to anhydrous salt by heating at 400°C.

Analysis

Elemental composition: Be 8.58%, S 30.51%, O 60.91%. The metal may be analyzed by various instrumental techniques (see Beryllium). Sulfate may be measured in the aqueous solution of the salt by gravimetric method (adding BaCl₂ solution and precipitating BaSO₄) or by ion chromatography.

Toxicity

The compound is acutely toxic by all routes of exposure, and a carcinogen. LD₅₀ oral (mouse): 50 mg/kg.

BISMUTH

[7440–69–9]

Symbol Bi; atomic number 83; atomic weight 208.98; a heavy metallic element of the nitrogen group in the periodic table; atomic radius 1.88Å (coordination number 12); ionic radii in crystals corresponding to coordination number 6: Bi³⁺ 1.03Å, Bi⁵⁺ 0.76 Å; atomic volume 21.3 cc/g-atom; electronic configuration [Xe] 4f¹⁴5d¹⁰6s²6p³; ionization potentials, Bi(+3) 25.56eV and Bi(+5) 56.0 eV; electron affinity 0.946 eV; electronegativity (Allred-Rochow type) 1.67; valence states +3, +5.

Occurrence and Uses

Bismuth occurs in nature in ores, bismite (Bi₂O₃), bismuth glance or bismuthinite (Bi₂S₃), tetradymite (a mixed sulfide and telluride), and also as carbonates in bismutite and bismutophaerite. It also is found in elemental form or native bismuth in small quantities associated with the ores of zinc, silver, tin and lead. The concentration of bismuth in the earth's crust is estimated to be in the range 8.5 x 10⁻³ mg/kg and in sea 20 ng/L (ppt). The major commercial applications of bismuth are in pharmaceuticals and as fusible alloys. Some bismuth compounds also find catalytic applications in the manufacture of acrylic fibers. It is used in electric fuses, fusible boiler plugs, low-melting solders, thermoelectric materials, and semiconductors, and as an additive to steel and other metals. Many bismuth compounds are used in medicine as antacids, antisyphilitics and anti-infectives; and in cosmetics such as lipsticks, powder and eye shadow.

Physical Properties

Grayish-white metal with pinkish tinge; high metallic luster; soft and brittle; rhombohedral crystal system (a= 4.7457Å, axial angle 57° 14.2'); density 9.79 g/cm³; hardness (Brinell) 7; melting point 271°C (contracts on melting, volume expansion on solidification 3.32%); vaporizes at 1,564°C; vapor pressure 10, 100 and 400 torr at 1,100, 1,200, and 1,400°C, respectively; poor conductor of electricity, electrical resistivity 106.8 and 160.2 microhm-cm at 0

and 100°C, respectively (higher in solid than in liquid state); greatest Hall effect (increase in resistance when placed in a magnetic field) among all metals; mass susceptibility -1.35×10^6 (highly diamagnetic).

Thermochemical Properties

$\Delta H^{\circ}f$ (g)	49.52 kcal/mol
$G^{\circ}f$ (g)	40.22 kcal/mol
S° (g)	44.7 cal/degree mol
C_p (g)	6.10 cal/degree mol
Specific heat (20°C)	0.0294 cal/g°C
Coeff. Lin. expansion	$13.3 \times 10^{-6}/^{\circ}\text{C}$
Thermal conductivity	
at 20°C	0.020 cal/sec/cm ³
at 250°C	0.018 cal/sec/cm ³
at 400°C	0.037 cal/sec/cm ³
ΔH_{fus}	2.70 kcal/mol
ΔH_{vap}	42.7 kcal/mol

Production

Bismuth is obtained as a by-product in smelting and refining of lead, copper or tungsten ores. The metal is partially volatilized when the ore is smelted at the high temperature. Separation from copper is achieved by electrolytic refining, bismuth accumulating in the anode slimes with lead, arsenic, antimony, tellurium, and other metal impurities. All throughout the smelting and refining operations bismuth accompanies lead. It finally is removed from lead by Betterton-Kroll or Betts processes. The Betterton-Kroll process involves the addition of calcium-lead alloy or magnesium metal to lead slime, thus converting bismuth to high-melting bismuthides of calcium or magnesium, Ca_3Bi_2 or Mg_3Bi_2 , respectively. These bismuthides liquate from the bath and are separated as dross. Bismuth dross is then melted in kettles forming $\text{Bi}_7\text{Mg}_6\text{K}_9$ which liquates to the top of the bath and is removed from the molten lead. Treatments with caustic soda finally produce the high quality bismuth.

In a modified process, potassium substitutes for calcium to form $\text{Bi}_7\text{Mg}_6\text{Ca}_9$ which liquates to the top of the bath and is removed from the molten lead. The Betts process is based on electrolytic refining using a solution of lead fluorosilicate and fluorosilicic acid. While lead is deposited on the cathode, bismuth goes to the anode where it is collected with other impurity metals. It is then filtered, dried, smelted, and further refined, depending on the purity desired. Impurities are removed by adding molten caustic and zinc, and finally by chlorination.

Bismuth may be obtained from other ores, too. The recovery process however, depends primarily on the chemical nature of the ores. For example, the sulfide ore requires smelting, carbon reduction, and the addition of iron (to decompose any bismuth sulfide present). Oxide ores, on the other hand, are treated with hydrochloric acid to leach bismuth from the mineral. The bismuth chloride solution is then diluted with water to precipitate bismuth oxy-

chloride. The precipitate is roasted with lime and charcoal. Satisfactory recovery of the metal from its carbonate ore may be achieved by both the above techniques.

Bismuth is sold in the form of rod, lump, powder, and wire.

Reactions

Bismuth forms trivalent and pentavalent compounds. The trivalent compounds are more common. Many of its chemical properties are similar to other elements in its group; namely, arsenic and antimony.

Bismuth is stable to both dry and moist air at ordinary temperatures. At elevated temperatures, the vapors of the metal combine rapidly with oxygen, forming bismuth trioxide, Bi_2O_3 . The element dissolves in concentrated nitric acid forming bismuth nitrate pentahydrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Addition of water to this salt solution precipitates an oxysalt, $\text{Bi}_2\text{O}_3\text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. Reaction with hydrochloric acid followed by evaporation of the solution produces bismuth trichloride, BiCl_3 .

Bismuth reacts with chlorine, bromine and iodine vapors forming chloride, bromide and iodide of the metal, respectively. Molten bismuth and sulfur combine to form bismuth sulfide, Bi_2S_3 .

Analysis

The metal in trace quantities may be analyzed by furnace or flame AA or by ICP emission or ICP/MS techniques. The solid or liquid sample is digested with nitric acid and the solution is diluted appropriately and analyzed. The element may also be determined in solid salts or mixtures by various x-ray methods.

Hazard

In powder form, the metal is pyrophoric. The toxicity of bismuth and its compounds is very low.

BISMUTH CHLORIDE

[7787-60-2]

Formula: BiCl_3 ; MW 315.34

Synonyms: bismuth trichloride

Uses

Bismuth chloride is used to prepare several other bismuth salts; as a catalyst in organic synthesis; and as a constituent in pigments and cosmetics.

Physical Properties

Yellowish-white crystalline solid; cubic crystals; hygroscopic; density 4.75

g/cm³; melts at 230°C; vaporizes at 447°C; vapor pressure 5 torr at 242°C; reacts with water; soluble in acids, alcohol and acetone.

Thermochemical Properties

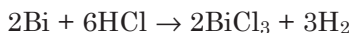
ΔH°_f	-117.3 kcal/mol
ΔG°_f	-106.6 kcal/mol
S°	19.8 cal/degree mol
C_p	15.5 cal/degree mol
ΔH_{fus}	2.61 kcal/mol
ΔH_{vap}	17.36 kcal/mol

Preparation

Bismuth chloride may be synthesized directly by passing chlorine over bismuth. Alternatively, the chloride salt may be prepared by adding hydrochloric acid to basic bismuth chloride and evaporating the solution:



Also, the compound can be prepared by dissolving bismuth in concentrated nitric acid and then adding solid sodium chloride into this solution. Another method of preparation is treating the metal with concentrated hydrochloric acid:



Analysis

Elemental composition: Bi 66.27%, Cl 22.73%. The metal may be analyzed by various instrumental techniques (see Bismuth). The solid salt may be identified nondestructively by x-ray methods.

BISMUTH HYDROXIDE

[10361-43-0]

Formula: $\text{Bi}(\text{OH})_3$; MW 260.00;

Synonyms: bismuth hydrate; hydrated bismuth oxide.

Uses

Bismuth hydroxide is used as an absorbent and in the hydrolysis of ribonucleic acid. It also is used in the isolation of plutonium from irradiated uranium.

Physical Properties

Yellowish-white amorphous powder; density 4.96 g/cm³; insoluble in water, soluble in acids; $K_{\text{sp}} 3.2 \times 10^{-40}$

Thermochemical Properties

ΔH°_f	-170.1 kcal/mol
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Preparation

Bismuth hydroxide is precipitated by adding sodium hydroxide to a solution of bismuth nitrate.

Analysis

Elemental composition: Bi 80.38%, H 1.16%, O 18.46%. See Bismuth.

BISMUTH NITRATE PENTAHYDRATE

[10035-06-0]

Formula: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; MW 485.07

Uses

The primary use of this compound is to produce a number of other bismuth compounds. It also is used in luminous paints and enamels; applied on tin to produce bismuth luster; and for precipitation of alkaloids.

Physical Properties

Lustrous triclinic crystals; acid taste; hygroscopic; density 2.83 g/cm³; decomposes at 75°C; reacts slowly with water; soluble in acids and acetone; insoluble in alcohol .

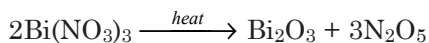
Preparation

Bismuth nitrate is prepared by dissolving bismuth in concentrated nitric acid, followed by evaporation and crystallization .

Reactions

Addition of water precipitates out an oxysalt, $\text{Bi}_2\text{O}_3\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$. The degree of hydrolysis and the product composition can vary with the amount of water and the reaction temperature .

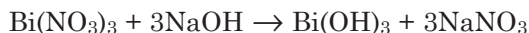
Thermal dissociation gives bismuth trioxide and dinitrogen pentoxide:



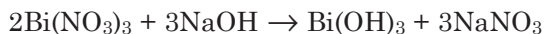
Bismuth nitrate reacts with gallic acid in glacial acetic acid to form bismuth subgallate, $\text{C}_6\text{H}_2(\text{OH})_3\text{COOBi}(\text{OH})_2$.

$\text{Bi}(\text{NO}_3)_3$ forms bismuth oxychloride, BiOCl in dilute nitric acid solution, upon addition of sodium chloride.

$\text{Bi}(\text{NO}_3)_3$ reacts with sodium hydroxide to form bismuth hydroxide, $\text{Bi}(\text{OH})_3$:



Reaction with potassium chromate produces bismuth chromate:



$\text{Bi}(\text{NO}_3)_3$ forms bismuth sulfide, Bi_2S_3 when hydrogen sulfide is passed through its solution in nitric acid.

BISMUTH OXYCHLORIDE

[7787-59-9]

Formula: BiOCl ; MW 260.43

Synonyms: bismuth chloride oxide; basic bismuth chloride; bismuth subchloride; bismuthyl chloride

Uses

Bismuth oxychloride is used in face powder and other cosmetics. It also is used in pigments; dry-cell cathodes; to make artificial pearls; and in medicines.

Physical Properties

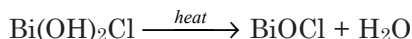
White powder or tetragonal crystals; density 7.72 g/cm³; practically insoluble in water, alcohol and acetone; soluble in hydrochloric and nitric acids (with decomposition); K_{sp} 7.0×10^{-9} .

Thermochemical Properties

ΔH°_f	-87.7 kcal/mol
ΔG°_f	-77.0 kcal/mol
S°	28.8 cal/degree mol

Preparation

Bismuth oxychloride is made by treating bismuth chloride with water and then drying the white precipitate so formed to expel a molecule of water:



Also, the compound is prepared by treating a dilute nitric acid solution of bismuth nitrate with sodium chloride.

Analysis

Elemental composition: Bi 80.24%, Cl 13.61%, O 6.14%. The metal may be analyzed by various instrumental techniques. (See Bismuth.)

BISMUTH OXYCARBONATE

[5892-10-4]

Formula: $(\text{BiO})_2\text{CO}_3$; MW 509.97

Synonyms: bismuth subcarbonate; bismuth carbonate, basic; bismuth basic

carbonate

Uses

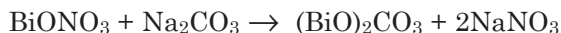
Bismuth oxycarbonate is used in cosmetics, enamel fluxes, ceramic glazes, plastic and artificial horn products. It also is used as an opacifier in x-ray diagnosis; and in medicine for treatment of gastric ulcers, diarrhea and enteritis.

Physical Properties

White powder; density 6.86 g/cm³; insoluble in water and alcohol; soluble in mineral acids.

Preparation

Bismuth oxycarbonate is prepared by adding sodium carbonate to a suspension of bismuth subnitrate in water.



(BiO)₂CO₃ also may be prepared by adding ammonium carbonate to a solution of bismuth salt. The nature of the product in the preparative processes depends on the nature of the subnitrate or the bismuth salt used, the amount of water and the temperature.

BISMUTH OXYNITRATE

[10361–46–3]

Formula: BiONO₃; MW 286.98

Synonyms: bismuth subnitrate; basic bismuth nitrate; bismuthyl nitrate; bismuth white

Uses

Bismuth oxynitrate is used in cosmetics, enamel fluxes and ceramic glazes. Medical applications include treatment of diarrhea, and gastric ulcers; and opacifier in x-ray diagnosis of alimentary canal .

Physical Properties

White powder; density 4.93 g/cm³; decomposes at 260°C; insoluble in water and ethanol; dissolves in acids.

Preparation

Bismuth oxynitrate is prepared by hydrolysis of bismuth nitrate using either water or sodium bicarbonate solution under mild heating (between 30 to 70°C) and stirring. The composition of the product formed can vary depending on the strength of nitric acid and the quantity of water used.

Reactions

At 260°C or above, bismuth oxynitrate decomposes to bismuth oxide and

oxides of nitrogen. The compound is practically insoluble in water. However, as a suspension in water, it reacts with many compounds, such as, sodium and other alkali metal bicarbonates, several soluble metal iodides and phosphates, and sulfur, forming precipitates of insoluble bismuth compounds.

BISMUTH SULFIDE

[1345–07–9]

Formula: Bi_2S_3 ; MW 514.16

Synonym: bismuth trisulfide

Occurrence and Uses

Bismuth sulfide occurs in nature as the mineral bismuthinite (bismuth glance). It is used as a starting material to produce many other bismuth compounds.

Physical Properties

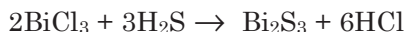
Brownish black orthogonal crystal; density 6.78 g/cm³; hardness 2 Mohs; melts at 850°C; insoluble in water; soluble in acids.

Thermochemical Properties

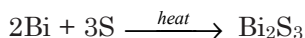
ΔH°_f	−34.22 kcal/mol
ΔG°_f	−33.62 kcal/mol
S°	47.9 cal/degree mol
C_p	29.2 cal/degree mol

Preparation

The compound occurs in nature as mineral bismuthinite. It can be prepared in the laboratory by passing hydrogen sulfide into a solution of bismuth chloride or any soluble bismuth salt:



Alternatively, bismuth sulfide may be obtained by melting a mixture of bismuth and sulfur:



Analysis

Elemental composition: Bi 81.29%, S 18.71%. The metal may be determined by digesting the compound in nitric acid followed by instrumental analysis (see Bismuth). Sulfur may be measured in the acid extract by ICP/AES technique.

BISMUTH TRIOXIDE

[1304–76–3]

Formula: Bi_2O_3 ; MW 465.96

Synonyms: bismuth oxide; bismite; bismuth yellow; bismuthous oxide

Occurrence and Uses

Bismuth trioxide occurs in nature as mineral bismite. The oxide is used in fireproofing of papers and polymers; in enameling cast iron ceramic; and in disinfectants.

Physical Properties

Yellow monoclinic crystal or powder; density 8.90 g/cm³; melts at 817°C; vaporizes at 1,890°C; insoluble in water; soluble in acids.

Thermochemical Properties

ΔH°_f	−137.2 kcal/mol
ΔG°_f	−118.1 kcal/mol
S°	36.2 cal/degree mol
C_p	27.1 cal/degree mol

Preparations

Bismuth trioxide is commercially made from bismuth subnitrate. The latter is produced by dissolving bismuth in hot nitric acid. Addition of excess sodium hydroxide followed by continuous heating of the mixture precipitates bismuth trioxide as a heavy yellow powder. Also, the trioxide can be prepared by ignition of bismuth hydroxide.

Reactions

Oxidation with ammonium persulfate and dilute caustic soda gives bismuth tetroxide, Bi_2O_4 . The same product can be obtained by using other oxidizing agents such as potassium ferricyanide and concentrated caustic potash solution.

Electrolysis of bismuth trioxide in hot concentrated alkali solution gives a scarlet red precipitate of bismuth pentoxide, Bi_2O_5 .

Bismuth trioxide reacts with hydrofluoric acid forming bismuth trifluoride, BiF_3 .

Reaction with acetic anhydride and oleic acid gives bismuth trioleate, $\text{Bi}(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$.

Analysis

Elemental composition: Bi 89.70%, O 10.30%. The compound may be analyzed by x-ray diffraction technique. Alternatively, it may be digested with nitric acid and the solution analyzed for Bi by AA or ICP spectrophotometry.

BORAX, ANHYDROUS

[1330-43-3]

Formula $\text{Na}_2\text{B}_4\text{O}_7$; MW 201.22

Synonyms: sodium tetraborate; disodium tetraborate; anhydrous borax

Uses

Anhydrous borax is used in the manufacture of glasses, glass wool, and metallurgical fluxes. Other uses are in enamels, frits, and glazes. It also is applied in fertilizers.

Physical Properties

Colorless glassy solid; also exists in several crystalline forms; hygroscopic; density 2.37 g/cm^3 (glassy form), 2.27 g/cm^3 (crystalline form); melts at 743°C ; vaporizes at $1,575^\circ\text{C}$; the α -form stable above 600°C ; dissolves slowly in cold water; soluble in methanol (16.7% as fine crystal), and ethylene glycol (30% as fine crystal).

Thermochemical Properties

ΔH°_f	-786.6 kcal/mol
ΔG°_f	-740.0 kcal/mol
S°	45.29 cal/degree mol
C_p	44.65 cal/degree mol
ΔH_{fus}	19.4 kcal/mol
ΔH_{soln}	-10.28 kcal/mol
$\Delta H_{\text{hydration}}$ (to decahydrate)	38.5 kcal/mol

Preparation

Anhydrous borax is made from its hydrated forms by calcination and fusion. In the United States, it is produced by US Borax and Kerr-McGee Corporations. The starting material is borax decahydrate. The amorphous form is obtained by rapid cooling of molten borax. The molten material on long standing produces the crystalline form.

Analysis

The B_2O_3 content of borax may be determined by extraction into HCl solution followed by complexation with mannitol and titration with dilute NaOH. The Na_2O content of borax may be measured by titration of an aqueous solution with dilute HCl. Boron and sodium metals in the acid extract of borax may be analyzed by atomic absorption or emission spectroscopy after appropriate dilution of the extract. In the solid phase B_2O_3 and Na_2O may be measured nondestructively by x-ray techniques.

Hazard

None

BORAX DECAHYDRATE

[1303-96-4]

Formula: $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; MW 381.37

Synonym: disodium tetraborate decahydrate

Occurrence and Uses

Borax decahydrate occurs in nature as mineral, borax (tincal). It is one of the most common sodium borate ores. The compound has several industrial applications. The refined material is mostly used in household cleaning products. It is used to make pyrex and other borosilicate glasses. Borax is added to fertilizers in small quantities as a source of boron, as a trace nutrient for plants. High purity grade borax is used in cosmetics, toilet products and electrolytic capacitors. It also is used in fire retardants, adhesives and herbicides.

Physical Properties

White monoclinic crystal; density 1.73 g/cm³; decomposes at 75°C; soluble in water; the vapor pressure of the pure compound 1.6 torr at 20°C and that of a saturated solution 130 torr at 58°C; the pH of a 1% aqueous solution 9.24 (the pH is nearly independent of concentration); readily dissolves in alcohols

Production

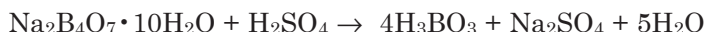
Borax decahydrate is produced from borate ores, primarily colemanite and also from dry lake brines. When produced from its ore, the ore is crushed and then blended with B_2O_3 . The blend is mixed with hot recycle liquor in a dissolving plant. Rock and clay particles from the liquor are removed over vibrating screens. The liquor is then fed to thickeners for settling of insolubles after which the underflow mud is washed with water. The strong liquor of borax hydrates is then pumped into continuous vacuum crystallizers for the separation of the pentahydrate first and then the decahydrate. The products are dried in rotary or fluid bed driers.

In most commercial processes, borax is obtained from lake brines, tincal and colemanite. The primary salt constituents of brine are sodium chloride, sodium sulfate, sodium carbonate and potassium chloride. The percent composition of borax as $\text{Na}_2\text{B}_4\text{O}_7$ in brine is generally in the range 1.5 to 1.6%. Borax is separated from these salts by various physical and chemical processes. The brine solution (mixed with mother liquor) is subject to evaporation and crystallization for the continuous removal of NaCl , Na_2CO_3 and Na_2SO_4 , respectively. The hot liquor consists of concentrated solution of potassium salts and borate components of the brine. The insoluble solid particles are filtered out and the liquor is cooled rapidly in continuous vacuum crystallizers under controlled conditions of temperatures and concentrations to crystallize KCl. Crystallization of borax along with KCl from the concentrated liquor must not occur at this stage. KCl is separated from the liquor by filtration. Bicarbonate then is added to the liquor to prevent any formation of sodium

metaborate. The liquor then is evaporated and refrigerated to crystallize borax.

Reactions

Reactions with acids and bases produce borates with varying $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratios. While acids produce borates with $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ mole ratios less than 0.5, their ratio is greater than 0.5 with bases. Treatment with sulfuric acid produces boric acid and sodium sulfate:



Reaction with hydrofluoric acid produces boron trifluoride, BF_3 .

Dehydration gives pentahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ and other lower hydrates. Calcination at elevated temperatures gives anhydrous borax.

Analysis

Water of crystalization can be analyzed by TGA or DTA methods. The theoretical water content of borax decahydrate is 47.2%. The salt is digested with acid and the boron and sodium content may be measured by AA or ICP spectrophotometry. The compound may be identified by x-ray methods.

BORAX PENTAHYDRATE

[12045–88–4]

Formula: $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$; MW 291.30

Synonyms: disodium tetraborate pentahydrate; sodium tetraborate pentahydrate; tincalconite (mineral)

Occurrence and Uses

Borax pentahydrate occurs in nature as mineral tincalconite, formed by dehydration of borax. It has several industrial applications, mostly the same as its decahydrate. The pentahydrate is used in the manufacture of borosilicate glass. It also is used in cleaning agents; ceramic glaze; adhesives; cosmetics; antifreeze; and herbicide formulations. It is added to fertilizers to provide boron as a nutrient to the plants.

Physical Properties

Hexagonal crystal; density 1.88 g/cm³; decomposes on heating; reversibly converts to an amorphous dihydrate when heated at 88°C at 2 torr; soluble in water (13% at 45°C), soluble in alcohols (17% in methanol and 31% in ethylene glycol by weight).

Thermochemical Properties

ΔH°_f	–273.3 kcal/mol
Specific heat	316 cal/g°C

Production

Borax pentahydrate is produced from various sodium borate and magnesium borate ores. In the United States, it is produced from dry lake brines, colemanite and tincal. It is commercially produced along with the decahydrate. The production processes are similar to decahydrate (see Borax decahydrate).

BORIC ACID

[10043-35-3]

Formula: $B(OH)_3$; MW 61.833;

Synonyms: orthoboric acid; boracic acid

Uses

Boric acid is used to prepare a variety of glasses including fiber glass, heat resistant borosilicate glass, and sealing glasses. It also is used to make porcelain. A major application of boric acid is to prepare a number of boron compounds including inorganic borate salts, boron halides, borate esters, fluoborates, and many boron alloys. The compound is used as a component of welding and brazing fluxes.

Boric acid is used as an antiseptic in mouthwashes, eye washes, and ointments; a preservative in natural products; to protect wood against insect damage; in washing citrus fruits; as a catalyst in hydrocarbon oxidation; as a flame retardant in cellulose insulation; in nickel electroplating baths; and as a buffer in ammonia analysis of wastewaters by acid titration.

Physical Properties

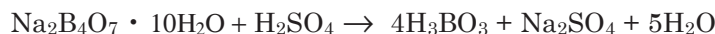
Colorless, transparent triclinic crystal or white granule or powder; density 1.435 g/cm³; melts at 171°C under normal heating; however, slow heating causes loss of water; sparingly soluble in cold water (4.7% at 20°C); pH of 0.1M solution 5.1; readily dissolves in hot water (19.1% at 80°C and 27.5% at 100°C); also soluble in lower alcohols and moderately soluble in pyridine.

Thermochemical Properties

ΔH_f° (cry)	-261.5 kcal/mol
ΔH_f° (gas)	-231.5 kcal/mol
ΔG_f° (cry)	-237.6 kcal/mol
S°	21.22 cal/degree mol
C_p	19.46 cal/degree mol

Preparation

Boric acid is produced from borax, colemanite, or other inorganic borates by reaction with sulfuric acid or hydrochloric acid, and cooling the solution to proper temperature:



It also may be prepared by extraction of weak borax brine with a kerosene solution of an aromatic diol, such as 2-ethyl-1,3-hexanediol or 3-chloro-2-hydroxy-5-(1,1,3,3-tetramethylbutyl)benzyl alcohol. The diol-borate chelate formed separates into a kerosene phase. Treatment with sulfuric acid yields boric acid which partitions into aqueous phase and is purified by recrystallization.

Reactions

In dilute aqueous solutions, the boric acid molecule remains undissociated B(OH)_3 ; but in concentrated solutions, B(OH)_4^- and complex polyborate anions, such as $\text{B}_3\text{O}_3(\text{OH})_4^-$ are formed. Reactions with fluoride ion produce fluoroborates, BF(OH)_3^- , $\text{BF}_2(\text{OH})_2^-$, $\text{BF}_3(\text{OH})^-$, BF_4^- , and $\text{B}_3\text{O}_3\text{F}_6^{3-}$ in stepwise sequence. It forms similar polyions with amides and borates.

Boric acid on slow heating loses water around 130°C , forming metaboric acid HBO_2 which converts into different crystal modifications that depend on the temperature. Further heating dehydrates metaboric acid to pyroboric acid, $\text{H}_2\text{B}_4\text{O}_7$ and boric oxide, B_2O_3 .

Boric acid forms complexes with a number of inorganic ions and organic molecules. Ammonia, hydrazine, hydroxides and oxyhalides form complexes with boric acid. The organics include diols, thiols, dioxane, pyridine and many other solvents in which boric acid dissolves.

Heating with metal oxides at elevated temperatures produces anhydrous borates. Reactions with halogens in the presence of carbon at temperatures above 500°C give boron trihalides. Heating a mixture of boric acid, ammonia and calcium phosphate in an electric furnace produces boron nitride.

Analysis

Elemental composition: B 17.50%, H 4.88%, O 77.62%. Boric acid may be analysed by adding calcium chloride (in excess) and sorbitol or mannitol to its solution, followed by acid-base titration using a strong base to phenolphthalein endpoint. Elemental boron may be analyzed by AA or ICP spectrophotometry.

BORIC OXIDE

[1303-86-2]

Formula: B_2O_3 ; MW 69.620

Synonyms: boric anhydride; boron oxide; diboron trioxide

Uses

Boric oxide is used to produce many types of glass including low-sodium, continuous filaments for glass-belted tires, and fiberglass plastics. It also is used to make ceramic coatings, porcelain enamels and glazes. Also, the compound is used as an acid catalyst in organic synthesis; and to prepare several other boron compounds.

Physical Properties

Colorless glassy solid or vitreous crystal; hexagonal crystal system; slightly bitter taste; hygroscopic; density 2.55 g/cm³; melts at 450°C; vaporizes at 1,500°C; slightly soluble in cold water (3.3%), soluble in alcohol and boiling water (20%).

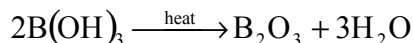
Thermochemical Properties

ΔH_f° (cry)	−304.4 kcal/mol
ΔH_f° (gas)	−201.7 kcal/mol
ΔG_f° (cry)	−285.4 kcal/mol
ΔG_f° (gas)	−198.9 kcal/mol
S° (cry)	12.9 cal/degree mol
S° (gas)	66.9 cal/degree mol
C_p (gas)	16.0 cal/degree mol

Preparation

Boric oxide is produced by treating borax with sulfuric acid in a fusion furnace. At temperatures above 750°C, the molten boric acid layer separates out from sodium sulfate. It then is decanted, cooled, and obtained in 96–97% purity. Boric acid above 99% purity may be obtained by fusing granular material.

Boric oxide may be prepared by heating boric acid:



Reactions

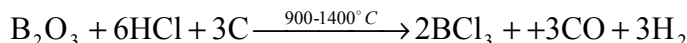
Boric oxide reacts with water forming boric acid:



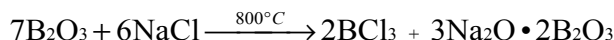
The reaction is exothermic (ΔH°_f hydration is −18.15 kcal/mol B_2O_3). In the molten state, it reacts with water vapor to form gaseous metaboric acid, HBO_2 .



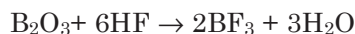
Reaction with hydrochloric acid or chlorine in the presence of carbon at elevated temperatures produces boron trichloride:



Similar reactions occur with many other chlorine-containing compounds, BCl_3 being produced (see Boron Trichloride reactions). Anhydrous borax and BCl_3 are obtained when it is heated with sodium chloride at 800°C:



Reaction with hydrofluoric acid produces boron trifluoride:



When heated in an electric furnace, B_2O_3 is reduced by carbon to form boron carbide, B_4C , and reacts with calcium phosphate and ammonia to form boron nitride, BN . It reacts with sulfuric acid to produce a borate derivative, $H[B(HSO_4)_4]$. It combines with several metal oxides to form mixed oxides when heated above $1,000^\circ C$.

BORON

[7440-42-8]

Symbol: B; atomic number 5; atomic weight 10.811; a Group III A (Group 13) metalloid element; atomic volume 4.70 cc/g-atom; electron affinity 0.277 eV; electronic configuration $1s^2 2s^2 2p^1$; valence state +3; naturally occurring stable isotopes are B-10 and B-11 and their abundance 19.57% and 80.43%, respectively.

Occurrence and Uses

The element was discovered in 1808 independently by Sir Humphrey Davy and also by GayLussac and Thenard. Boron does not occur in nature in free elemental form but is found in many borate ores. The principal borate minerals are as follows:

sassolite	[10043-35-3],	$B(OH)_3$
borax (tincal)	[1303-96-4],	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$
kernite	[12045-87-3],	$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$
tincalconite	[12045-88-4],	$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$
colemanite	[12291-65-5],	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$
ulexite	[1319-33-1],	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$
probertite	[12229-14-0],	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 10H_2O$
hydroboracite	[12046-12-7],	$CaO \cdot MgO \cdot 3B_2O_3 \cdot 6H_2O$
szaibelyite	[12447-04-0],	$2MgO \cdot B_2O_3 \cdot H_2O$

The major borate minerals found in the United States are tincal, kernite, brine, colemanite, ulexite and probertite. Boron also is found in many volcanic spring waters. Its abundance in the earth's crust is estimated to be 0.001%, and in seawater 4.4 mg/L

The most important application of boron is to make fibers or whiskers of single crystal or ceramic crystal. The addition of boron to metals, alloys, or other solids, imparts resistance to plastic flow, and thereby produces unusual strength in the material. Amorphous boron is used in rockets as an igniter, and in pyrotechnic flares to give green color. Many boron compounds, such as borax, boron hydrides, and boron halides, have important commercial applications (see individual compounds).

Physical Properties

Black hard solid or brownish black amorphous powder; also occurs as tetragonal, α -rhombohedral and β -rhombohedral crystal forms; density 2.34 g/cm³ (crystal), 2.45 g/cm³ (amorphous powder); hardness 9.3 Mohs; melts at $2,075^\circ C$; vaporizes at $4,000^\circ C$; electrical resistivity 3,000,000 ohm-cm at

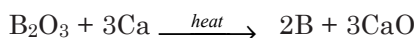
100°C.

Thermochemical Properties

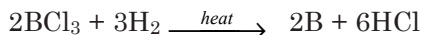
$\Delta H_f^\circ(\text{gas})$	135.1 kcal/mol
$G_f^\circ(\text{gas})$	124.6 kcal/mol
$S^\circ(\text{gas})$	36.68 cal/degree mol
$C_p(\text{gas})$	4.97 cal/degree mol
ΔH_{fus}	12.0 kcal/mol
ΔH_{vap}	114.8 kcal/mol

Preparation

Boron may be prepared by several methods, such as chemical reduction of boron compounds, electrolytic reduction in nonaqueous phase, or by thermal decomposition. Many boron compounds including boron oxides, borates, boron halides, borohydrides, and fluoroborates can be reduced to boron by a reactive metal or hydrogen at high temperatures:



The metal is obtained as a black amorphous product.



High purity grade boron may be prepared by such hydrogen reduction at high temperatures using a hot filament.

Electrolytic reduction and thermal decomposition have not yet been applied in large scale commercial methods. Electrolysis of alkali or alkaline earth borates produces boron in low purity. Electrolytic reduction of fused melts of boron trioxide or potassium tetrafluoroborate in potassium chloride yield boron in high purity. Also, boron tribromide or boron hydrides may be thermally dissociated by heating at elevated temperatures.

Impurities from boron may be removed by successive recrystallization or volatilization at high temperatures. Removal of certain impurities such as oxygen, nitrogen, hydrogen or carbon from boron are more difficult and involve more complex steps.

Reactions

Reactivity of boron is relatively much lower than practically all other metals in the periodic table. Also, reactivity varies with physical state and particle size of the element: the micron amorphous form is more reactive than the crystalline modifications. The element exhibits +3 oxidation state in most of its compounds.

Boron does not react with water at ambient temperatures. The powdered amorphous form, however, reacts slowly at 100°C producing boric acid. The amorphous metal reacts slowly with dilute mineral acids at ambient temperatures; the crystalline form is inert. The former, however, reacts vigorously with concentrated nitric acid. The amorphous powder ignites in oxygen at

700°C.

Boron reacts with halogens to form boron halides. The reaction is instantaneous with fluorine but occurs at elevated temperatures with other halogens. With chlorine, bromine and iodine, the formation of halides completes around 400°C, 600°C and 900°C, respectively. Again, the amorphous powder of the metal is more reactive than the crystalline form.

Boron combines with nonmetals at elevated temperatures. It readily combines with oxygen at 1,000°C forming boron oxide, B_2O_3 ; with hydrogen around 850°C, producing diborane and other boron hydrides; and with nitrogen at red heat forming boron nitride, BN. It also combines with carbon at high temperatures to give boron carbide B_4C . It reacts with B_2O_3 at above 1,000°C to form boron monoxide and suboxides of various compositions.

Boron combines with refractive metals forming their borides; e.g., AlB_{12} , SiB_6 , CrB_2 , ZrB_2 , and TiB_2 . Many of these borides have important industrial applications. Most reactions occur at temperatures in the range 1,100°C to 2,000°C. The reactions are exothermic and can be rapid.

Analysis

Boron may be analyzed by various instrumental methods, such as atomic absorption (AA) and atomic emission spectrophotometry (ICP/AES). Individual isotopes at an exceedingly trace concentration in solution phase may be measured by ICP/MS. The later method should be preferred over the AA techniques.

Also, boron can be analyzed by colorimetry techniques (APHA, AWWA, and WEF, 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington DC: American Public Health Association). Boron in acidified aqueous phase reacts with curcumin to form a red-colored product, rosocyanine. Presence of calcium and magnesium at high concentrations can interfere in the test. Another colorimetric measurement involves the reaction of boron with carmine or carminic acid in concentrated sulfuric acid. The color of the solution changes from bright red to bluish red or blue, depending on boron concentration.

Toxicity

Boron in the elemental form is nontoxic. Rubbing the amorphous powder on the skin can produce irritation. Some compounds of boron, however, are poisonous (see under individual compounds).

BORON CARBIDE

[12069–32–8]

Formula: B_4C ; MW 55.255

Uses

Boron carbide is used in sandblast nozzles, ceramic armor plates and abrasive powder grinding wheels. Because of its high neutron absorptivity and

chemical inertness, it also is used as a shielding material in nuclear reactors.

Physical Properties

Black hard crystal; density 2.50 g/cm³; hardness 9.3 Mohs; melts at 2,350°C; vaporizes above 3,500°C; insoluble in water and acid; inert to most chemicals at ordinary temperatures; rapidly attacked by hot alkalis.

Preparation

Boron carbide is prepared by reduction of boric oxide either with carbon or with magnesium in presence of carbon in an electric furnace at a temperature above 1,400°C. When magnesium is used, the reaction may be carried out in a graphite furnace and the magnesium byproducts are removed by treatment with acid.

BORON HYDRIDES

Boron forms a class of binary compounds known as boron hydrides or boranes with hydrogen (Numbers in parentheses are the number of hydrogen atoms in each compound.) The names, CAS Numbers, and formulas of some of these compounds are:

diborane(6)	[19287-45-7]	B ₂ H ₆
tetraborane(10)	[18283-93-7]	B ₄ H ₁₀
pentaborane(9)	[19624-22-7]	B ₅ H ₉
pentaborane(11)	[19433-84-6]	B ₅ H ₁₁
hexaborane(10)	[23777-80-2]	B ₆ H ₁₀
nonaborane(15)	[19465-30-6]	B ₉ H ₁₅
decaborane(14)	[17702-41-9]	B ₁₀ H ₁₄

Uses

Boron hydrides are used in rocket propellants. They are ideal water-reactive fuels, liberating high energy when exposed to moist air or traces of water. Two other major applications of these compounds are in preparative chemistry, to produce borohydrides and many organoboranes, and as reducing agents. These substances find limited applications in catalysis. Diborane is a polymerization catalyst for olefins. Some minor applications of these compounds include vulcanization of rubber, corrosion inhibition, dye stripping, mothproofing, and as fluxing agents. Diborane also is used as a doping agent for p-type semiconductors.

Physical Properties

Diborane(6) and tetraborane(10) are colorless gases at ambient temperature and pressure. Diborane has a repulsive odor. Higher boranes up to nine boron atoms are colorless liquids. Decaborane(14) is a colorless crystalline solid. Pentaborane(11) and hexaborane(12) are unstable compounds. The densities and melting and boiling points of selected boron hydrides are shown in the following table:

boranes	densities g/mL	mp °C	bp °C
diborane(6)	1.214 g/L	-165.5	-92.4
tetraborane(10)	2.34 g/L	-121	18
pentaborane(9)	0.60	-46.6	60
pentaborane(11)	—	-123	63
hexaborane(10)	0.67	-62.3	108 (decomposes)
hexaborane(12)	—	-82	80
nonaborane(15)	2.6	—	—
decaborane(14)	0.94	99.6	213

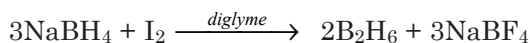
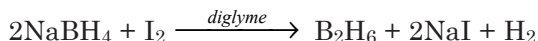
Boron hydrides are soluble in carbon disulfide, diglyme and ethyl acetate. They react with water.

Thermochemical Properties

borane(BH ₃)	ΔH_f°	23.9 kcal/mol
diborane(6)	ΔH_f°	8.509 kcal/mol
	ΔG_f°	20.72 kcal/mol
	S°	55.47 cal/degree mol
	C_p	13.6 cal/degree mol
	ΔH_{vap} at bp	3.41 kcal/mol
tetraborane(10)	ΔH_f°	15.798 kcal/mol
	ΔH_{vap} at bp	6.477 kcal/mol
pentaborane(9)	$\Delta H_f^\circ(\text{l})$	10.206 kcal/mol
	$\Delta H_f^\circ(\text{g})$	17.495 kcal/mol
	$\Delta G_f^\circ(\text{l})$	41.06 kcal/mol
	$\Delta G_f^\circ(\text{g})$	41.826 kcal/mol
	$S^\circ(\text{g})$	44.02 cal/degree mol
	$C_p(\text{g})$	36.11 cal/degree mol
pentaborane(11)	$\Delta H_f^\circ(\text{l})$	17.495 kcal/mol
	$\Delta H_f^\circ(\text{g})$	24.69 kcal/mol
	ΔH_{vap} at bp	7.60 kcal/mol
hexaborane(10)	$\Delta H_f^\circ(\text{l})$	13.456 kcal/mol
	$\Delta H_f^\circ(\text{g})$	22.61 kcal/mol
decaborane(14)	$\Delta H_f^\circ(\text{s})$	7.529 kcal/mol
	$\Delta G_f^\circ(\text{s})$	51.649 kcal/mol
	$S^\circ(\text{s})$	84.37 cal/degree mol

Preparation

Diborane is prepared by the reaction of sodium borohydride with iodine or boron trifluoride or trichloride in diglyme:

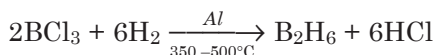


It also may be prepared by the reaction of sodium borohydride with sulfu-

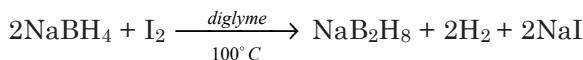
ric acid:



Diborane also can be made by reduction of boron trichloride with either sodium hydride at room temperature in diglyme or with hydrogen over aluminum at 350 to 500°C :



Tetraborane too can be prepared from sodium borohydride. The reaction, however, is carried out at a high temperature. The product sodium octahydroborate is treated with hydrochloric acid to yield tetraborane:

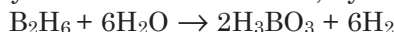


Higher boranes can be produced from diborane by pyrolysis.

Reactions

Boranes oxidize in air to form boron oxides. Diborane spontaneously ignites in air around 50°C. The presence of impurities can lower the ignition temperature. Tetraborane decomposes slowly at ordinary temperatures but rapidly on heating. Decaborane is very stable at ordinary temperatures. When heated at 300°C, it slowly decomposes to boron and hydrogen. All boranes decompose to their elements at elevated temperatures.

Boron hydrides react with water, hydrolyzing to boric acid and hydrogen:

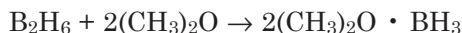


Decaborane is soluble in cold water but hydrolyzed in hot water.

Reactions with halogens give boron halides. While reaction with chlorine can be explosive with diborane, it is slow with bromine. Diborane reacts with alkanes forming alkylboranes. Reactions with aromatics give arylboranes.

Boranes undergo a variety of reactions, such as proton abstraction, electrophilic substitution, fragmentation and adduct formation. Some of these reactions are highlighted below with selective examples.

Lewis bases such as ammonia cleave boron hydrides unsymmetrically into BH_2^- and $\text{B}_{(n-1)}\text{H}_{(m-1)}^-$ fragments:



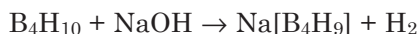
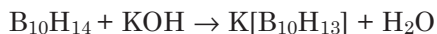
Alkali metal hydrides react with diborane to form metal borohydrides:



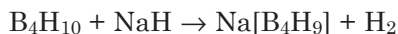
Decaborane reacts with pyridine, triphenyl phosphine, triethylamine, acetonitrile and other weak bases forming an adduct with liberation of hydrogen:



Deuterium exchange studies on decaborane and other boranes indicate acidic character of bridge hydrogens. They react with bases undergoing proton abstraction reactions:

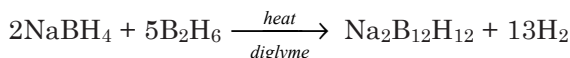


Alkali metal hydrides too abstract protons from boranes. While water is produced with basic hydroxides, hydrogen is liberated with hydrides. Except diborane, all other boron hydrides undergo similar reactions, liberating hydrogen:



Many boron hydrides, especially the higher boranes, undergo halogenation, alkylation and other substitution reactions when treated with electrophiles. Such reactions are catalyzed by acids, yielding a variety of stable products.

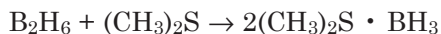
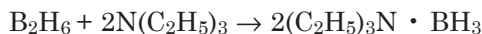
Diborane and other lower boranes pyrolyze when treated with borohydrides and other metallo borane derivatives at elevated temperatures undergoing polyhedral expansion:



Similarly, $[\text{B}_3\text{H}_8]^-$ pyrolyze at 230°C forming $[\text{B}_9\text{H}_9]_2^-$, $[\text{B}_{10}\text{H}_{10}]_2^-$, and

$[\text{B}_{12}\text{H}_{12}]_2^-$ borane anions.

Diborane forms stable adducts with many electron donors:



Boranes react with carbon monoxide forming more than one adduct:



Analysis

Diborane in air may be analyzed by passing air through a PTFE filter and oxidizer-impregnated charcoal. It is oxidized to boron and desorbed with 3% H_2O_2 . Boron is measured by plasma emission spectrometry or ICP emission spectrometry (NIOSH, 1984. *Manual of Analytical Methods*, 3rd ed. Cincinnati, OH: National Institute for Occupational Safety and Health). Boron hydrides can be analyzed by FTIR techniques.

Hazard

Diborane ignites spontaneously in moist air. Its flash point is in the range 38 to 52°C, and it forms explosive mixtures with air over a wide range: the lower and upper flammable limits are 0.8 to 88% by volume in air, respectively. Diborane explodes in contact with chlorine and ignites with fuming nitric acid. All boron hydrides react violently with halogenated extinguishing agents.

Exposure to boron hydride gases or vapors can cause irritation of respiratory passages, acute poisoning of lungs, and pulmonary edema. Ingestion of decaborane can cause spasm, tremor, and convulsion. For decaborane, LD₅₀ oral (mouse) is 41 mg/kg; LD₅₀ skin (mouse) is 740 mg/kg; and LC₅₀ inhalation (40 hr.) (mouse) is 12 ppm.

BORON NITRIDE

[10043-11-5]

Formula: BN; MW 24.818

Uses

Boron nitride is extremely hard and very resistant to both chemical attack and thermal shock. Because of these properties, BN has many industrial applications. Cubic crystals of boron nitride under the name Borazon are incorporated into abrasive wheels for grinding nickel and ferrous alloys. They also are used to make cutting tools for other hard alloys. The hexagonal crystal form is applied to construct refractory materials, such as vessels, crucibles, rectifying tubes, transistor mounting wafers, specialized equipment, and heatshields for plasma that need high temperature electrical and thermal insulation. Boron nitride is used to make heat resistant, high strength fibers.

Physical Properties

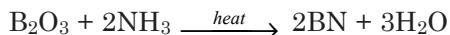
White powder, hexagonal graphite-like form or cubic crystal; cubic form similar to diamond in its crystal structure, and reverts to graphite form when heated above 1,700°C; density 2.18 g/cm³; melts at 2,975°C (under nitrogen pressure); sublimates at 2,500°C at atmospheric pressure; insoluble in water and acid; attacked by hot alkalis and fused alkali carbonates; not wetted by most molten metals or glasses.

Thermochemical Properties

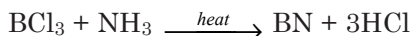
ΔH_f° (cry)	-60.80	kcal/mol
ΔG_f° (cry)	-54.59	kcal/mol
S° (cry)	3.54	cal/degree mol
C_p (cry)	4.71	cal/degree mol
ΔH_f° (g)	154.8	kcal/mol
ΔG_f° (g)		146.9 kcal/mol
S° (g)	50.74	cal/degree mol
C_p (g)	7.05	cal/degree mol

Preparation

Boron nitride is prepared by heating boric oxide with ammonia:



Alternatively, the compound can be prepared by heating boric oxide or boric acid with ammonium chloride or an alkali metal cyanide. Purified product can be obtained by high temperature reaction of boron halide with ammonia:



Boron nitride can also be made from the elements by heating boron and nitrogen at red heat.

BORON PHOSPHATE

[13308–51–5]

Formula: BPO_4 ; MW 105.784

Synonym: borophosphoric acid

Uses

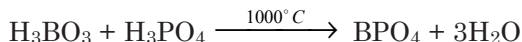
Boron phosphate is used as an acid catalyst for dehydration of alcohols to olefins; isomerization of olefins; nitration of aromatic hydrocarbons; polymerization of aldehydes and other synthetic reactions. It also is used as a flux in silica-based porcelain and ceramics; special glasses; and acid cleaners.

Physical Properties

White infusible solid; density 1.873 g/mL; sublimes slowly above 1,450°C; soluble in water, decomposes to phosphoric acid and boric acid; pH of 1% solution is ~2.0.

Preparation

Boron phosphate is prepared by heating an equimolar mixture of boric acid and phosphoric acid at 1,000 to 1,200°C:



Various preparative methods are adopted at nonstoichiometric formulations, incomplete dehydration or using oxide additives to obtain boron phosphate of varying purity for its catalytic applications. The compound also forms hydrates (tri-, tetra-, penta-, and hexahydrates) which readily decompose in water to phosphoric acid and boric acid.

Analysis

Elemental composition: B 10.22% ; P 29.28% ; O 60.50%. A small, measured

amount is dissolved in water and the solution is analyzed for orthophosphate by ion chromatography, or by molybdenum-blue colorimetric method (APHA, AWWA and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th. ed. Washington, DC: American Public Health Association). Borate may be analyzed by ion chromatography, and elemental boron by AA or ICP spectrophotometry, following appropriate dilution of the solution (see Boron).

BORON TRICHLORIDE

[10294–34–5]

Formula: BCl_3 ; MW 117.17; planar geometry; Cl–B–Cl bond angle 120°C ; a Lewis acid, an electron deficient compound.

Synonym: boron chloride

Uses

Boron trichloride is used as a catalyst in polymerization reactions. Other applications include refining of alloys; soldering flux; and as a component in certain fire extinguishers. It also is used to prepare boron fibers and other boron compounds including diborane, sodium borohydride and several adducts.

Physical Properties

Colorless gas (or fuming liquid); density 5.14 g/L; liquefies at 12.6°C ; solidifies at -107°C ; vapor pressure 470 torr at 0°C ; critical temperature 182°C ; critical pressure 38.2 atm; critical molar volume $239\text{ cm}^3/\text{mol}$; reacts with water and ethanol; soluble in carbon tetrachloride.

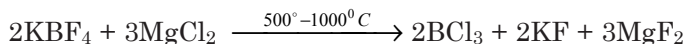
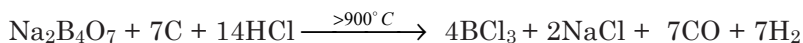
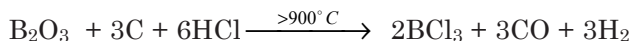
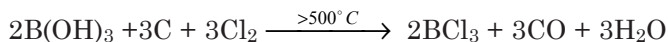
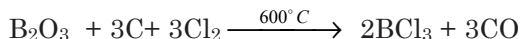
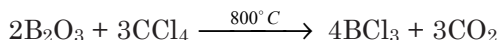
Thermochemical Properties

ΔH_f° (l)	–102.1	kcal/mol
ΔH_f° (g)	–96.5	kcal/mol
ΔG_f° (l)	–92	kcal/mol
ΔG_f° (g)	–92.9	kcal/mol
S° (l)	49.3	cal/degree mol
S° (g)	69.3	cal/degree mol
C_p (l)	25.5	cal/degree mol
C_p (g)	15.0	cal/degree mol
ΔH_{vap}	5.68	kcal/mol
ΔH_{fus}	0.50	kcal/mol

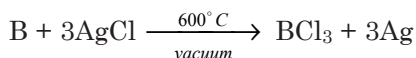
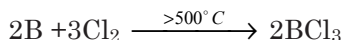
Preparation

Boron trichloride can be prepared by high temperature chlorination of boron trioxide, boric acid, metal borates or other boron compounds. Chlorine, hydrogen chloride, phosgene, silicon tetrachloride, metal chlorides, carbon

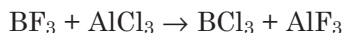
tetrachloride, sulfuryl chloride and phosphorus tri- and pentachlorides are some of the common chlorinating agents. The reaction is carried out at temperatures varying between 400° to 1,400°C, depending on the reactants used. In commercial processes, carbon is generally used to reduce boron oxide during its chlorination. Some of the preparative reactions are outlined below:



Boron trichloride may also be obtained by high temperature chlorination of boron:

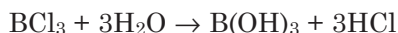


In the laboratory, boron trichloride may be made at ordinary temperatures by the reaction of boron trifluoride with aluminum chloride:

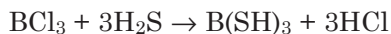


Reactions

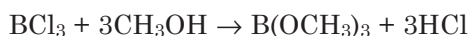
Boron trichloride reacts with water forming boric acid and hydrogen chloride:



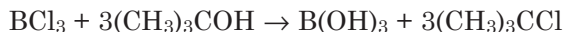
Similar reaction occurs with hydrogen sulfide:



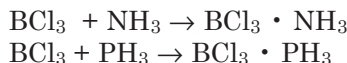
Reaction with lower alcohols produces alkyl derivatives of boric acid with hydrogen chloride:



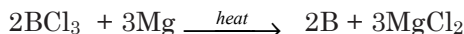
However, tertiary alcohol gives alkyl chloride and no HCl is produced:



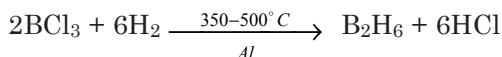
At low temperatures, donor-acceptor complexes are obtained with Lewis bases; for example, with ammonia and phosphine, the adducts are boron trichloride ammonia and boron trichloride phosphine, respectively:



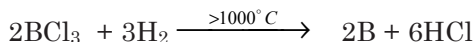
Sodium, potassium, magnesium and other alkali and alkaline earth metals at elevated temperatures reduce boron trichloride to elemental boron:



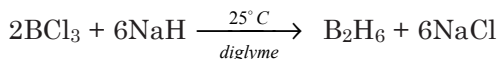
Hydrogen reduces the compound to diborane when heated at 350 to 500°C over aluminum:



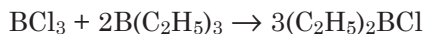
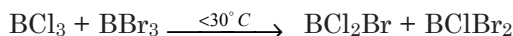
but at higher temperatures over 1,000°C, hydrogen decomposes boron trichloride forming boron fibers and HCl:



Alkali metal hydrides reduce boron trichloride to diborane at ordinary temperatures:



Boron trichloride undergoes several exchange reactions with diborane, other boron halides and trialkyl-, triaryl-, or triaryloxy boranes (Lower, L.D. 1978. Boron compounds (halides). In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd. ed. pp 129–135. New York: Wiley Interscience). The reactions occur at ambient or lower temperatures:



Analysis

Elemental composition: B 9.23%, Cl 90.77%. The compound is slowly hydrolyzed (reaction may be vigorous to violent) and the solution is analyzed for boron by AA or ICP spectroscopy (see Boron). Also, other metals that may be present as impurities can be measured. The product, HCl in the aqueous solution, resulting from hydrolysis, may be analyzed by chloride ion-selective

electrode or ion chromatography (at trace concentrations) with appropriate dilution.

Toxicity

Boron trichloride is highly toxic, causing severe irritation of eyes, skin and mucous membranes.

LC_{LO} inhalation (rat): 20 ppm/7hr.

BORON TRIFLUORIDE

[7637-07-2]

Formula: BF₃; MW 67.82; planar sp² hybridization; F–B–F angle 120°; an electron deficient compound (Lewis acid)

Synonym: boron fluoride

Uses

Boron trifluoride is used as a catalyst in esterification, polymerization and many other organic synthetic reactions. Other applications of this compound include measuring weak neutrons in ionization chambers and in devices to monitor radiation levels in the earth's atmosphere; and measuring depth for oil drilling. It also is used in fumigation; as a flux for soldering magnesium; to prepare diborane; and in gas brazing.

Physical Properties

Colorless gas; pungent suffocating odor; density 2.975 g/L; fumes in moist air; liquefies at –101°C; solidifies at –126.8°; vapor pressure at –128°C is 57.8 torr; critical temperature –12.2°C; critical pressure 49.15 atm; critical volume 115 cm³/mol; soluble in water with partial hydrolysis; solubility in water at 0°C 332 g/100g; also soluble in benzene, toluene, hexane, chloroform and methylene chloride; soluble in anhydrous concentrated sulfuric acid.

Thermochemical Properties

ΔH_f°	–271.5 kcal/mol
ΔG_f°	–267.5 kcal/mol
S°	60.8 cal/degree mol
ΔH_{vap}	4.62 kcal/mol
ΔH_{fus}	1.004 kcal/mol

Preparation

Boron trifluoride is prepared by treating borax with hydrofluoric acid; or boric acid with ammonium bifluoride. The complex intermediate product is then treated with cold fuming sulfuric acid.

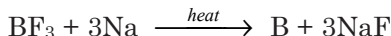
Reaction

Boron trifluoride is partially hydrolyzed when dissolved in water. The hydrolysis products are boric acid and fluoroboric acid:



The tetrafluoroborate, BF_4^- anion can form stable salts with pyridinium, tetraalkylammonium and other countercations.

Boron trifluoride is reduced to elemental boron when heated with alkali metals:



The reaction is highly exothermic resulting in incandescence. Similar reduction occurs with alkaline earth metals except magnesium.

Being an electron deficient compound, boron trifluoride forms complexes with Lewis bases and compounds that have unshared pair(s) of electrons. With ammonia, it forms boron trifluoride ammonia. Similar coordination compounds are formed with monoethylamine, $\text{BF}_3\text{-NH}_2\text{C}_2\text{H}_5$; diethyl ether, $\text{CH}_3\text{CH}_2\text{O}(\text{BF}_3)\text{CH}_2\text{CH}_3$; and methanol, $\text{BF}_3\text{-OHCH}_3$. It forms a solid complex $\text{HNO}_3\text{-2BF}_3$ with concentrated nitric acid.

BORON TRIFLUORIDE ETHERATE

[109–63–7]

Formula: $(\text{CH}_3\text{CH}_2\text{O})_2\text{O} \cdot \text{BF}_3$; MW 141.94;

Synonyms: boron fluoride etherate; boron fluoride ethyl ether

Uses

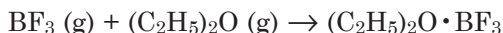
Boron trifluoride etherate is used as a catalyst in many organic reactions; namely, alkylation, polymerization and condensation reactions.

Physical Properties

Fuming liquid; stable at ambient temperatures but hydrolyzed on exposure to moist air; density 1.125 g/mL; refractive index 1.348; solidifies at -60.4°C ; boils at 125.7°C ; flash point (open cup) 147°F (68.8°C); decomposes in water.

Preparation

Boron trifluoride etherate is prepared by the reaction of vapors of boron trifluoride with that of anhydrous diethyl ether:

**Toxicity**

The compound is highly toxic by inhalation. Skin contact causes burns.